

- 1974, 30, 1579-1586.
- (5) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory," McGraw-Hill: New York, 1970.
- (6) (a) Epiotis, N. D.; Cherry, W. *J. Chem. Soc., Chem. Commun.* **1973**, 278-279. (b) Hoffmann, R.; Levin, C. C.; Moss, R. A. *J. Am. Chem. Soc.* **1973**, 95, 629-631. (c) Hehre, W. J.; Salem, L. *J. Chem. Soc., Chem. Commun.* **1973**, 754-755. (d) Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, 95, 3087-3096. (e) Cremer, D.; Binkley, J. S.; Pople, J. A.; Hehre, W. J. *ibid.* **1974**, 96, 6900-6903. (f) Epiotis, N. D.; Yates, R. L.; Bernardi, F. *ibid.* **1975**, 97, 5961-5970. (g) Hehre, W. J.; Pople, J. A. *ibid.* **1975**, 97, 6941-6955. (h) Bernardi, F.; Epiotis, N. D.; Yates, R. L.; Schlegel, H. B. *ibid.* **1976**, 98, 2385-2390.
- (7) Theilacker, W.; Berger-Brose, U.; Beyer, K. H. *Chem. Ber.* **1960**, 93, 1658-1681.
- (8) Cristol, S. J.; Pennelle, D. K. *J. Org. Chem.* **1970**, 35, 2357-2361.
- (9) The time during the present pulse train was sufficiently shorter than T_1 (min) [Wind, R. A.; Emdin, S.; Pourquié, J. F. J. M.; Smidt, J. *J. Chem. Phys.* **1977**, 67, 2436-2442].
- (10) Mansfield, P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1971**, 8, 54-66.
- (11) (a) Stejskal, E. O.; Gutowsky, H. S. *J. Chem. Phys.* **1958**, 28, 388-396. (b) Woessner, D. E. *ibid.* **1962**, 36, 1-4.
- (12) (a) Anderson, J. E.; Slichter, W. P. *J. Phys. Chem.* **1965**, 69, 3099-3104. (b) Stohrer, M.; Noack, F. *J. Chem. Phys.* **1977**, 67, 3729-3738.
- (13) (a) Polak, M.; Sheinblatt, M. *J. Magn. Reson.* **1973**, 12, 261-269. (b) McDowell, C. A.; Raghunathan, P.; Williams, D. S. *ibid.* **1976**, 24, 113-123.
- (14) Oki, M. *Angew. Chem., Int. Ed. Engl.* **1976**, 15, 87-93.
- (15) Weiss, S.; Lerol, G. *J. Chem. Phys.* **1968**, 48, 962-967.
- (16) (a) During, J. R.; Bucy, W. E.; Wurrey, C. J. *J. Chem. Phys.* **1974**, 60, 3293-3298. (b) Zens, A. P.; Ellis, P. D. *J. Am. Chem. Soc.* **1975**, 97, 5685-5688.
- (17) von Schütz, J. U.; Noack, F. *Z. Naturforsch. A* **1972**, 27, 645-651.
- (18) (a) Palmer, K. J.; Templeton, D. H. *Acta Crystallogr., Sect. B* **1968**, 24, 1048-1052. (b) Karle, I. L.; Estlin, J. A. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1969**, 128, 371-389. (c) Anzenhofer, K.; de Boer, J. J. *ibid.* **1970**, 131, 103-113.
- (19) Of course, only one methyl H eclipses torsional C owing to a slight tilt of the C₁₇-C₉ bond for 2.
- (20) Payne, P. W.; Allen, L. C. "Applications of Electronic Structure Theory," Schaefer III, H. F., Ed.; Plenum Press: New York, 1977; p 46.
- (21) Too large rotational barriers are obtained if the MM1 transition state geometries are used, e.g., 23.02 kcal/mol for 1.
- (22) Similar values, 5.04 and 3.79 kcal/mol for 1 and 2, are obtained by the MINDO/3 method [Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, 97, 1285-1293].
- (23) (a) Gordon, M. S. *J. Am. Chem. Soc.* **1969**, 91, 3122-3130. (b) Kollmar, H.; Smith, H. O. *Theor. Chim. Acta* **1971**, 20, 65-79.
- (24) Reference 20, p 67.
- (25) Because of the neglect of overlaps in the CNDO/2 method, repulsive interactions between occupied orbitals are eliminated.

Internal Rotation in Biacetyl. A Theoretical Study

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Abstract: The internal rotation about the central C-C bond in biacetyl has been investigated using both semiempirical and ab initio molecular orbital techniques. The results indicate that, while both trans and cis conformers can exist, the latter is present to less than 1% at room temperature. This result is in agreement with experimental studies in which only the trans conformer was observed. The highest occupied molecular orbitals are the n_a , π_b , n_b , and π_a orbitals in order of increasing Koopmans' theorem ionization potentials.

Introduction

The 1,2-dicarbonyls (OXCCXO) have been the subject of extensive experimental and theoretical study. These investigations have concentrated on determining the barrier to internal rotation about the central C-C bond and on the ordering of the highest occupied molecular orbitals. Glyoxal (OHC-CHO) has been shown to exist predominantly in the trans form^{1,2} but there is also experimental evidence for the existence of a cis planar structure.^{3,4} The existence of both planar trans and cis conformers for glyoxal was confirmed by the ab initio calculations of Dykstra and Schaefer,⁵ who found a trans-cis energy separation of 5.9 kcal/mol and a barrier to internal rotation of 7.5 kcal/mol with respect to the trans structure. They also determined the ordering of the highest occupied molecular orbitals to be n_a , π_b , n_b , π_a in order of increasing ionization potential (Koopmans' theorem). Kanev and Tyutyulkov⁶ used a semiempirical PPP(CI) procedure on trans-glyoxal to show that the antibonding 1A_g and 1B_g levels crossed when singly or polyexcited configurations were considered and on this basis changed the assignment of the 43 000-cm⁻¹ band of glyoxal from a charge transfer to a symmetry-forbidden 1A_g transition. Oxalyl fluoride (OFCCFO) has also been shown spectroscopically⁷ to exist in the trans and cis planar forms and this has been confirmed theoretically⁸ with the trans structure again being the dominant form. The ordering of the highest occupied molecular orbitals in oxalyl fluoride was found to be identical with that in glyoxal, though the n_b and π_a orbitals are nearly degenerate in energy. Spectroscopically⁹ oxalyl chlorofluoride

(OCICCFO) has been identified only in the planar trans form, but ab initio calculations⁸ suggest that a planar cis form should also exist and again indicate an orbital ordering of n , π , n , π . The experimental evidence on oxalyl chloride (OCICCCIO) is somewhat contradictory suggesting either dominant trans and less stable cis forms¹⁰ or a dominant trans and a less abundant gauche form.¹¹ Ab initio calculations⁸ support the latter result but give an orbital ordering, in the trans form, of n_a , n_b , π_b , π_a , though the latter three orbitals are nearly degenerate.

Biacetyl or 2,3-butanedione (OCH₃CCCH₃O) was investigated by Hagen and Hedberg¹² using electron-diffraction methods and no evidence was found for anything other than the trans conformer. Their conclusion was that, if any other forms were present, they must be in amounts less than 10%. They obtained a value of $V^* = V_1 + 4V_2 + 9V_3 = 11.4$ kcal/mol. These results were in good agreement with earlier spectroscopic investigations.¹³ Henderson and Meyer¹⁴ carried out dipole-moment measurements on biacetyl in solution, pure liquid, and vapor phases and their results again show the presence of only the trans conformer. Their value for $V^* = 7.60$ kcal/mol was somewhat lower than that obtained by Hagen and Hedberg.¹² Sidman and McClure¹⁵ investigated the electronic spectra of biacetyl and concluded that the ordering of the highest occupied molecular orbitals was n_a , n_b , π_b , π_a with the n orbitals being degenerate.

The purpose of this study is to investigate the ground-state structure of biacetyl with particular attention being paid to the internal rotation potential and to determine whether more than

Table I. Biacetyl Optimized Geometries and Total Energies as a Function of the OCCO Dihedral Angle^a

	0° ^b	30°	60°	90°	120°	150°	180°
R _{C=O}	1.209 (1.214)	1.210	1.210	1.209	1.208	1.207	1.206
R _{C-C}	1.543 (1.507)	1.539	1.531	1.530	1.535	1.543	1.550
R _{C-CH₃}	1.497 (1.527)	1.497	1.498	1.498	1.500	1.501	1.503
R _{C-H}	1.110 (1.114)	1.110	1.109	1.109	1.109	1.109	1.109
∠CCO	120.6 (120.3)	121.0	121.7	121.9	120.9	119.2	118.9
∠CCC	117.4 (116.3)	117.5	117.7	118.5	119.1	119.9	119.9
∠CCH	114.4 (108.1)	114.6	115.0	115.2	115.3	115.1	115.2
total energy, eV	-1219.0559	-1219.0962	-1219.1656	-1219.1604	-1219.0400	-1218.8815	-1218.8077

^a Using MINDO/3 program. Bond lengths in angstroms and bond angles in degrees. ^b Figures in parentheses are experimental geometries.¹²

Table II. Biacetyl Total Energies^a as a Function of OCCO Dihedral Angle

dihedral angle, deg	MINDO/3 optimized geometries	exptl geometry (rigid rotor)
0 (trans)	-302.913 09	-302.919 61
30	-302.912 23	-302.917 99
60	-302.910 35	-302.914 73
90	-302.909 16	-302.912 43
120	-302.909 49	-302.911 92
150	-302.910 18	-302.912 76
180 (cis)	-302.910 61	-302.912 57

^a Energies are in hartrees (1 hartree = 627.5 kcal/mol).

one conformer exists. In addition the ordering of the highest occupied molecular orbitals will be obtained and compared with previous predictions for biacetyl and other 1,2-dicarbonyls.

Method and Results

Biacetyl was initially studied using the MINDO/3 program of Dewar et al.¹⁶ giving optimized geometries and total energies for a range of dihedral angles as shown in Table I. These same optimized geometries were then used in the GAUSSIAN 70¹⁷ ab initio program with an STO-4G basis set to again determine the total energies as a function of the dihedral OCCO angle and the results are given in Table II. The experimental geometry obtained by Hagen and Hedberg¹² was used with the STO-4G basis set and the GAUSSIAN 70 program, but treating the molecule as a rigid rotor, to again determine the variation of total energy with dihedral angle and these results are also shown in Table II. Table III indicates the variation in the nuclear repulsion and total electronic energies as a function of the dihedral angle. Finally Table IV gives the ordering of the highest occupied molecular orbitals in the trans conformer as obtained using ab initio procedures with the MINDO/3 optimized geometry and with the experimental geometry.

Discussion

A comparison of the MINDO/3 optimized geometry for the trans conformer and the experimental geometry of Hagen and Hedberg¹² in Table I indicates the major discrepancies to be in the central C-C bond length, which is calculated to be too long by about 0.04 Å, in the C-CH₃ bond length, which is 0.03 Å too short, and in the CCH angle, which is too large by almost 6°. The other calculated parameters are in reasonably good agreement with experiment. The fact that the calculated values for the central C-C bond and for the C=O bond are respectively too large and somewhat small suggests that the MINDO/3 procedure overemphasizes localized π bonding in the carbonyl groups while underemphasizing conjugation between these groups. The longer calculated central C-C bond should lead to a lower nuclear repulsion energy and less vari-

Table III. Nuclear Repulsion and Total Electronic Energies^a as a Function of Dihedral Angle

dihedral angle, deg	MINDO/3 optimized geometries		exptl geometry (rigid rotor)	
	nuclear repulsion	total electronic	nuclear repulsion	total electronic
0 (trans)	224.8519	-527.7650	225.7664	-528.6860
30	224.7720	-527.6842	225.4518	-528.3698
60	224.6167	-527.5270	224.8475	-527.7622
90	224.5106	-527.4198	224.6047	-527.5171
120	224.4560	-527.3655	225.0273	-527.9392
150	224.4963	-527.4065	225.7751	-528.6879
180 (cis)	224.4603	-527.3709	226.1503	-529.0629

^a All energies are in hartrees.

Table IV. Biacetyl Molecular Orbitals^a in Trans Conformer

GAUSSIAN 70 (MINDO/3 optimized geometry)	GAUSSIAN 70 (exptl geometry)
-0.3118 n _a	-0.3086 n _a
-0.3934 π _b	-0.3944 π _b
-0.4061 n _b	-0.4059 n _b
-0.4501 π _a	-0.4526 π _a

^a Energies are in hartrees. Subscripts a and b indicate symmetry or antisymmetry, respectively, with respect to rotation about C₂ axis.

ation in this energy with changing dihedral angle as compared to the situation where the experimental geometry is used. This is in fact observed as indicated in Table III. Bock et al.¹⁸ have compared the geometry-optimized structures of ethylene, formaldehyde, *trans*-1,3-butadiene, and *trans*- and *cis*-glyoxal. Their conclusion was that the calculated value for the C-C bond length in *trans*-glyoxal (1.498 Å) was more realistic than the electron-diffraction value (1.525 Å). This would suggest the experimental value for the central C-C bond in biacetyl (1.507 Å) to be reasonable or at worst an upper limit. There is almost no change in either the CCH angle or the C-H bond length for the MINDO/3 optimized geometries as the OCCO dihedral angle is varied. The C=O and C-CH₃ bonds also undergo only minor changes in bond length with changing dihedral angle. The central C-C bond length does, however, vary significantly, initially decreasing as the dihedral angle goes from 0° to 90° and then steadily increasing to a maximum in the *cis* conformer (dihedral angle = 180°). A somewhat similar pattern is observed for the CCO angle, which first increases till a 90° dihedral structure is reached and then falls to a minimum in the *cis* structure. There is also an overall increase in the CCC angle observed in going from the *trans* (0°) to the *cis* (180°) structures.

The change in the total energy in the MINDO/3 calculations as a function of dihedral angle leads to a minimum in

energy at a dihedral angle of 74° and energy maxima at the trans and cis positions with the former being at a lower energy (more negative). This is not consistent with any of the experimental data but is a well-established feature of calculations using the CNDO, INDO, or MINDO type of approximations. Gropen and Seip¹⁹ have shown in a number of instances including glyoxal and 1,3-butadiene that the CNDO method leads to energy minima in twisted conformations and seems to minimize the stabilizing effect of conjugation. Preliminary calculations on oxalyl fluoride and oxalyl chloride by the writer, using the CNDO method, show a preference for the cis over the trans conformer in opposition to experimental evidence. However, when these MINDO/3 optimized geometries are used in ab initio calculations with an STO-4G basis set a more reasonable picture (when compared to experimental data) of the internal rotation potential is obtained. Minima are observed for both the trans and cis conformers with an energy difference of 1.56 kcal/mol in favor of the trans conformer. This would correspond to less than 7% cis conformer at 298 K and is thus in agreement with Hagen and Hedberg's¹² conclusion that, if any conformer other than the trans conformer were present, it would be at a level of less than 10%. The barrier to internal rotation from the trans conformer is 2.53 kcal/mol and the barrier top corresponds to a dihedral angle of 97° .

When the ab initio STO-4G basis set calculations were repeated using the experimental geometry and treating biacetyl as a rigid rotor a lower energy is obtained for all conformations and particularly the trans conformer. The observed shape of the internal rotation potential is similar to that obtained using the MINDO/3 optimized geometries in an ab initio calculation. There is, however, a flattening or very slight upturn in the energy at the cis conformation which is probably a function of treating the molecule as a rigid rotor. The overall shape of the potential does, however, indicate minima for the trans and cis structures with an energy separation of 4.42 kcal/mol in favor of the former. This energy difference would indicate that there is less than 0.1% of the cis conformer present at 298 K, which is even more supportive of the lack of experimental evidence for the existence of a cis conformer. The barrier to internal rotation from the trans conformer is 4.87 kcal/mol and the barrier top is at a dihedral angle of 112° .

The internal rotation potential in biacetyl can be described in terms of a Fourier expansion, $2V(\phi) = \sum_n V_n(1 - \cos n\phi)$, where ϕ is the dihedral angle, truncated either after the second or third term. This expansion will be used to examine the data obtained using the experimental geometry, rigid rotor model and with the trans structure chosen as the zero-energy form. If a two-term expansion is used, employing the values for $V(\phi)$ at $\phi = 60$ and 120° the results for V_1 and V_2 are 3.52 and 2.91 kcal/mol, respectively. The value for V^* is then 15.16 kcal/mol, which is somewhat larger than the 11.4 kcal/mol obtained by Hagen and Hedberg.¹² This would also give a value for $V(\phi)$ at $\phi = 180^\circ$ of 3.52 kcal/mol corresponding to only 0.25% of the cis form being present at 298 K. If a three-term expansion is used the resulting values of V_1 , V_2 , and V_3 are respectively 4.32, 2.11, and 0.40 kcal/mol and V^* is now 16.36 kcal/mol. The three-term Fourier expansion gives a shallower minimum

for the cis conformer with a value of $V(\phi)$ at $\phi = 180^\circ$ of 4.72 kcal/mol and therefore essentially no cis conformer present at 298 K. It is clear that the V_1 and V_2 terms are the dominant contributors to the internal rotation potential of biacetyl with the former particularly so in the three-term expansion. The V_1 term indicates the increasing importance of steric repulsion in going from the trans to the cis conformer. The V_2 term emphasizes the enhanced stability of the planar over the non-planar forms presumably because of the increased degree of conjugation in the planar structures.

Recent ab initio calculations on glyoxal⁵ and on the oxalyl halides⁸ would tend to support the ordering of the highest occupied molecular orbitals in biacetyl as being n_a , π_b , n_b , π_a in order of increasing Koopmans' theorem ionization potential and the results listed in Table IV using both the MINDO/3 optimized geometry and the experimental geometry are in full agreement with this. They are, however, somewhat in disagreement with the predictions of Sidman and McClure,¹⁵ who suggested an ordering n_a , n_b , π_b , π_a with the n_a and n_b orbitals degenerate. It should be noted, however, that the π_b and n_b orbitals are nearly degenerate in energy so that the ordering of these orbitals is not clear-cut, but it is also obvious that the n_a and n_b orbitals are not degenerate. These results do suggest that, while the lowest energy electronic transition is likely to be $n \rightarrow \pi^*$, there is also the possibility of finding $\pi \rightarrow \pi^*$ transitions among the $n \rightarrow \pi^*$ ones.

These ab initio calculations would therefore indicate that, while there is a theoretical possibility of a cis conformer of biacetyl, it has no significant abundance at room temperature in agreement with experimental conclusions. The calculations also confirm the ordering of the highest occupied molecular orbitals to be n_a , π_b , n_b , π_a , in order of increasing Koopmans' theorem ionization potential, in agreement with the results obtained by ab initio calculations on other 1,2-dicarbonyls.

References and Notes

- (1) J. C. D. Brand, *Trans. Faraday Soc.*, **50**, 431 (1954).
- (2) J. Paldus and D. A. Ramsay, *Can. J. Phys.*, **45**, 1389 (1967).
- (3) G. N. Currie and D. A. Ramsay, *Can. J. Phys.*, **49**, 317 (1971).
- (4) J. R. Durig, C. C. Tong, and Y. S. Li, *J. Chem. Phys.*, **57**, 4425 (1972).
- (5) C. E. Dykstra and H. F. Schaefer, *J. Am. Chem. Soc.*, **97**, 7210 (1975).
- (6) I. Kanev and N. Tyutyulkov, *Dokl. Bolg. Akad. Nauk*, **29**, 217 (1976).
- (7) J. R. Durig, S. C. Brown, and S. E. Hannum, *J. Chem. Phys.*, **54**, 4428 (1971).
- (8) J. Tyrrell, *J. Am. Chem. Soc.*, **98**, 5456 (1976).
- (9) J. Goubeau and M. Adelhelm, *Spectrochim. Acta, Part A*, **28**, 2471 (1972).
- (10) J. R. Durig and S. E. Hannum, *J. Chem. Phys.*, **52**, 6089 (1970).
- (11) K. Hagen and K. Hedberg, *J. Am. Chem. Soc.*, **95**, 1003 (1973).
- (12) K. Hagen and K. Hedberg, *J. Am. Chem. Soc.*, **95**, 8266 (1973).
- (13) J. R. Durig, S. E. Hannum, and S. C. Brown, *J. Phys. Chem.*, **75**, 1946 (1971).
- (14) G. L. Henderson and G. H. Meyer, *J. Phys. Chem.*, **80**, 2422 (1976).
- (15) J. W. Sidman and D. S. McClure, *J. Am. Chem. Soc.*, **77**, 6461 (1955).
- (16) M. J. S. Dewar, H. Metiu, P. J. Student, A. Brown, R. C. Bingham, D. H. Lo, C. A. Ramsden, H. Kollmar, P. Weiner, and P. K. Bischof, MINDO/3: General IBM Version, modified by M. L. Olson and J. F. Chiang, QCPE No. 309, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
- (17) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, GAUSSIAN 70, QCPE No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
- (18) C. W. Bock, P. George, G. J. Mains, and M. Trachtman, *J. Mol. Struct.*, **49**, 211 (1978).
- (19) O. Gropen and H. M. Seip, *Chem. Phys. Lett.*, **11**, 445 (1971).